

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 11 September 2000 (11.09.00)	
International application No. PCT/EP00/00160	Applicant's or agent's file reference PP/W-21904/A/AC 515
International filing date (day/month/year) 12 January 2000 (12.01.00)	Priority date (day/month/year) 26 January 1999 (26.01.99)
Applicant DONNELLY, Simon et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

04 August 2000 (04.08.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Juan Cruz

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PP/W-21904/A/AC 515	<div style="display: flex; justify-content: space-between;"> <div style="text-align: center;"> FOR FURTHER ACTION </div> <div style="font-size: small;"> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. </div> </div>	
International application No. PCT/EP 00/ 00160	International filing date (day/month/year) <div style="text-align: center;">12/01/2000</div>	(Earliest) Priority Date (day/month/year) <div style="text-align: center;">26/01/1999</div>
Applicant CIBA SPECIALTY CHEMICALS WATER TREATMENTS ...ET AL		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

EP 00/00160

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 D21H23/02 D21H17/37 D21H17/41 C08F2/24 //D21H21/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 197 (C-128), 6 October 1982 (1982-10-06) & JP 57 108103 A (DAINIPPON INK & CHEM INC;OTHERS: 01), 6 July 1982 (1982-07-06) abstract	22, 26
Y	----	1, 17, 22
Y	DE 30 47 688 A (BASF AG) 22 July 1982 (1982-07-22) the whole document	1, 17, 22
A	----	3, 4, 7-12, 16, 18-20, 25, 26
	----- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 March 2000

Date of mailing of the international search report

17/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
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Authorized officer

Nestby, K

INTERNATIONAL SEARCH REPORT

International Application No

EP 00/00160

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 904 727 A (PROBST JOACHIM ET AL) 27 February 1990 (1990-02-27) the whole document	1, 17
A		10-12, 14-16, 18, 20
Y	EP 0 400 410 A (BAYER AG) 5 December 1990 (1990-12-05) the whole document	1, 17
A		10-12, 14-16, 18, 20, 21
Y	DATABASE PAPERCHEM 'Online! THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY, ATLANTA, GA, US O'BRIEN, J. T: "OLIGOMERIC SURFACTANTS AND DISPERSANTS - A REVIEW" retrieved from DIALOG XP002132202 abstract	1, 17, 22
A	& PULP PAPER CAN. 77, NO. 11: 83-86 'T215-T218! (NOV. 1976).,	2, 8, 10, 18
Y	DE 26 04 547 A (BASF AG) 11 August 1977 (1977-08-11) the whole document, in particular paragraph bridging pages 12, 13 ("Dispersion 9")	1
A		10-15
A	US 3 498 943 A (DANNALS LELAND E) 3 March 1970 (1970-03-03)	
A	EP 0 320 594 A (NIPPON CATALYTIC CHEM IND ; OJI PAPER CO (JP)) 21 June 1989 (1989-06-21)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP 00/00160

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 57108103	A	06-07-1982	JP 1749086 C JP 4032083 B	08-04-1993 28-05-1992
DE 3047688	A	22-07-1982	NONE	
US 4904727	A	27-02-1990	DE 3718520 A NL 8801421 A	15-12-1988 02-01-1989
EP 0400410	A	05-12-1990	DE 3917647 A DE 59008824 D JP 3024106 A	06-12-1990 11-05-1995 01-02-1991
DE 2604547	A	11-08-1977	AU 2149777 A FR 2340401 A IT 1083187 B JP 52096209 A SE 7701060 A	27-07-1978 02-09-1977 21-05-1985 12-08-1977 07-08-1977
US 3498943	A	03-03-1970	AT 298058 B BE 697914 A CH 476035 B CH 497518 B CH 534769 A CH 541660 B DE 1745507 A DK 139683 B ES 351376 A ES 351377 A FI 48099 B FR 1521995 A GB 1207532 A JP 53005282 B LU 53581 A NL 6706262 A, B NO 130904 B NO 129403 B SE 369724 B SE 362081 B SE 358883 B US 3668230 A US 3772382 A US 3776874 A	15-03-1972 03-11-1967 31-07-1969 15-10-1970 15-02-1973 31-10-1973 16-03-1972 26-03-1979 01-12-1969 01-12-1969 28-02-1974 14-08-1968 07-10-1970 25-02-1978 03-05-1967 06-11-1967 25-11-1974 08-04-1974 16-09-1974 26-11-1973 13-08-1973 06-06-1972 13-11-1973 04-12-1973
EP 0320594	A	21-06-1989	JP 1183582 A JP 1678862 C JP 3043386 B JP 1203438 A JP 1770139 C JP 4059336 B JP 1203449 A JP 2592885 B JP 1221402 A JP 2013630 C JP 7035405 B JP 1292179 A JP 1700083 C JP 3045140 B JP 1156335 A	21-07-1989 13-07-1992 02-07-1991 16-08-1989 30-06-1993 22-09-1992 16-08-1989 19-03-1997 04-09-1989 02-02-1996 19-04-1995 24-11-1989 14-10-1992 10-07-1991 19-06-1989

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP 00/00160

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0320594 A		JP 1156376 A	19-06-1989
		JP 7002928 B	18-01-1995
		DE 3888644 D	28-04-1994
		DE 3888644 T	25-08-1994
		US 5087603 A	11-02-1992
		US 5284900 A	08-02-1994
		JP 2029383 A	31-01-1990
		JP 2050465 C	10-05-1996
		JP 7084099 B	13-09-1995

REC'D 30 APR 2001


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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 21904/AC515		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/00160	International filing date (day/month/year) 12/01/2000	Priority date (day/month/year) 26/01/1999	
International Patent Classification (IPC) or national classification and IPC D21H23/02			
Applicant CIBA SPECIALTY CHEMICALS WATER TREATMENTS ...ET AL			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <p>I <input checked="" type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input checked="" type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>			
Date of submission of the demand 04/08/2000		Date of completion of this report 26.04.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Nestby, K Telephone No. +49 89 2399 8625	



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00160

I. Basis of this report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):
- Description, pages:**

1-25 as originally filed

Claims, No.:

1-26 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00160

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-26
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-26
Industrial applicability (IA)	Yes:	Claims	1-26
	No:	Claims	

2. Citations and explanations see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/00160

R Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1: JP-A-57 108103 (available as abstract only)

D2: DE-A-30 47 688

D3: US-A-4 904 727

D4: EP-A-0 400 410

D5: Paperchem abstract 4 708 924 concerning article by O'Brien J. T. "Oligomeric surfactants and dispersants - a review" Pulp Paper Canada 77, no. 11, Nov. 1976, pages 83-86.

D6: DE-A-26 04 547

D7: US-A-3 498 943

2. The document D1 is regarded as being the closest prior art to the subject-matter of claim 22, and it discloses:

A composition comprising an emulsion produced by polymerising ethylenically unsaturated monomer(s) in the presence of an oligomer formed from a monomer blend comprising

A3) 0-85 mole % ethylenically unsaturated monomer, e. g. acrylamide;

A4) 1-40 mole % of an organic thiol, e. g. n-octyl mercaptan;

A2) 5-90 mole % of a cationic ethylenically unsaturated monomer, e. g. vinylpyridine; and

A1) 5-90 mole % of an anionic ethylenically unsaturated monomer, e. g. acrylic acid.

- 2.1 The subject-matter of claim 22 therefore differs from this known emulsion in that firstly the dispersion comprises particles (with water insoluble polymer matrix) of size up to 1 micron, and secondly that said oligomer is located at the surface of the particles.

Although these features are not explicitly mentioned in the abstract, it cannot be excluded that they are comprised in the complete specification of D1. In any case,

said features proposed in claim 22 of the present application cannot be considered as involving an inventive step (Article 33(3) PCT) for the following reasons.

The polymer particles of the composition of claim 22 indicates a conventional latex as disclosed in the documents D2 to D7, see in particular D3, column 9, lines 20-23 and D4, page 6, second paragraph ("particle size of 15-200 nm"). Therefore, if not already disclosed in the complete D1 specification, this would be obvious from said prior art.

As to the second distinguishing feature, the examiner assumes that it is inherent from the prior art that at least some emulsifying agent (oligomer) must be located at the surface of latex particles during polymerisation. In fact, it follows from the description of the present application that no particular measures are taken to ensure that the oligomer is located at the surface of the particles, see in particular pages 16, 17 and the examples ("Emulsion polymerisation is effected in the usual manner").

3. Any of the documents D2, D3, D4, D5 may be regarded as being the closest prior art to the subject-matter of claim 17 since they pertain to the application of oligomers with or without sizing agents to paper.

When starting from D2 as closest prior art this document describes, see in particular pages 17, 18, a method of improving printability (see Table 2: "Tintendurchschlag") of a sheet of paper by applying to the surface of the paper a composition comprising an oligomer (see claim 1) formed from a monomer blend comprising an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group (see claim 2) and (meth)acrylamide (see page 7, line 31).

- 3.1 The subject-matter of claim 17 differs therefrom only in that the oligomer comprises an organic mercaptan or sulphone.

Since the examples of the application are based on starch/polymer blends **without comparison** with compositions/emulsions not comprising the particular oligomers of the present application, advantages (if any) with regard to the prior

art as disclosed in D1 to D7 are not apparent.

Therefore, the problem to be solved by the subject-matter of claim 17 (as well as claims 1, 22) can therefore be regarded as adding to the state of the art further methods (compositions) having the same effects as those already known.

The solution proposed in claim 17 of the present application cannot be considered as involving an inventive step (Article 33(3) PCT) for the following reasons.

Oligomer formed from blends comprising also an organic mercaptan or sulphone are known from D1, D5, D7. At least according to D5 it is known to apply said oligomers to paper.

Said distinguishing feature is hence merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed, thereby arriving at the subject-matter of claim 17 without having to exercise any inventive skill.

4. By the same token, the method of claim 1 disclosing sizing in the mass in addition to surface sizing cannot be considered as involving an inventive step (Article 33(3) PCT) either, in particular with regard to D5 alone ("oligomeric emulsifiers and deposition aids for beater-added latexes") or in combination with the documents D2, D3, D6.
5. Dependent claims 2 to 16, 18 to 21, 23 to 26 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step, because said features would appear to be conventional, see inter alia D2, D3, D4 (blends of sizing agents with starch), D6 (copolymer of styrene/2-ethylhexyl acrylate as sizing agent: see example 9), etc.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/00160

R l t m VII

Certain defects in the international application

6. A document reflecting the prior art described on page 1 (third paragraph), is not identified in the description (Rule 5.1(a)(ii) PCT). D7 could be used for this purpose.
7. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1, D2, D3, D4, D5, D6 is not mentioned in the description, nor are these documents identified therein.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : D21H 23/02, 17/37, 17/41, C08F 2/24 // D21H 21/16	A1	(11) International Publication Number: WO 00/44983 (43) International Publication Date: 3 August 2000 (03.08.00)
(21) International Application Number: PCT/EP00/00160 (22) International Filing Date: 12 January 2000 (12.01.00) (30) Priority Data: 9901597.6 26 January 1999 (26.01.99) GB (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED [GB/GB]; Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): DONNELLY, Simon [GB/GB]; 26 Pasture Road, Baildon, Shipley, West Yorkshire BD17 6QP (GB). STOCKWELL, John, Robert [GB/GB]; 21 Low Bank, Embsay, Skipton, North Yorkshire BD23 6SQ (GB). PLONKA, John [GB/GB]; 9 Derby Road, Rawden, Leeds, West Yorkshire LS19 6JB (GB). (74) Common Representative: CIBA SPECIALTY CHEMICALS WATER TREATMENTS LIMITED; Patents Department, Cleckheaton Road, Low Moor, Bradford, West Yorkshire BD12 0JZ (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: AQUEOUS POLYMERIC EMULSION COMPOSITIONS AND THEIR USE FOR THE SIZING OF PAPER		
(57) Abstract A method of sizing paper by applying a composition comprising an aqueous dispersion of polymeric particles of particle size up to 1 micron, preferably 80–200 nm, wherein the polymeric particles comprise a water insoluble polymer matrix, preferably formed from styrene and 2-ethylhexyl acrylate, characterised in that an oligomer formed from a monomer blend comprising, (a) (meth)acrylamide, and (b) organic mercaptan or an organic sulphone, preferably dodecyl mercaptan or dodecyl sulphone is located at the surface of the particles. Compositions where the oligomer further comprises an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, preferably dimethylaminoethymethacrylate are novel. Advantages of the composition when applied to the surface of paper, include improved water resistance, brightness and printability properties of the treated paper.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
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Aqueous Polymeric Emulsion Compositions and their Use for the Sizing of Paper

The present invention relates to novel compositions comprising an aqueous dispersion of water insoluble polymer particles, wherein the polymer particles further comprise at their surface an oligomeric compound. The invention also encompasses a method of sizing paper and a method for improving the printability of paper.

It is known to produce dispersions of water insoluble polymer particles by emulsion polymerisation or by suspension polymerisation. In such processes it would be usual to disperse a water insoluble monomer or monomer blend into an aqueous continuous phase to form droplets of monomer. In aqueous emulsion polymerisation or aqueous suspension polymerisation it is standard practice to use surface active ingredients such as emulsifiers, surfactants or polymerisation stabilisers. Typically such compounds would have a high Hydrophilic Lipophilic Balance (HLB) so that the compound would partition preferentially in the aqueous continuous phase.

It is known to use oligomeric compounds as emulsifiers or polymerisation stabilisers in the emulsion polymerisation of water insoluble monomers such as styrene, acrylonitrile, ethyl acrylate and butyl acrylate and the like. Such compositions have been produced as rubber or plastic latexes from which the solid polymer could be obtained. Generally such compositions were produced in order to provide products that exhibited low viscosity and reduced foaming characteristics and yet were able to form suitable solid rubber or plastic materials.

It is standard practice in the field of paper and board manufacture to both internally and externally size paper. The sizing agent imparts hydrophobicity to the paper or paper board and improves the resistance to penetration by liquids, especially water. Internal sizing is normally achieved by incorporating a sizing agent into the paper making stock prior to draining on the machine wire. The sizing agent may be a non-reactive size such as rosin, but more usually is a reactive size such as alkenyl succinic anhydride (ASA). ASA would easily be dispersed throughout the cellulosic suspension and chemically reacts with the cellulose and is therefore generally

regarded as a very efficient sizing agent. However, due to the reactivity of ASA size, and the ease with which it easily hydrolyses the aqueous sizing emulsions are normally made up in situ. If hydrolysis of the ASA anhydride groups take place to any significant degree before application, this could result in gummy deposits which would damage paper formation and in severe cases stop paper production. Therefore care has to be taken when applying reactive size.

It is known to use various hydrophobic materials such as waxes and water insoluble polymers and reactive sizes, such as ASA as paper surface sizing compositions. Generally such compositions are prepared as aqueous dispersions or emulsions and are blended with other materials such as starch prior to being applied to the paper sheet at the size press. It is important to impart the right degree of hydrophobicity and thus water resistance without impairing the brightness of the paper. It is often the case that a product that imparts optimum hydrophobicity significantly reduces brightness. Often it is necessary to strike a compromise between hydrophobicity and brightness and the product that is chosen does not impair brightness too significantly and yet provides adequate water resistance. Where products provide maximum water resistance to the paper, the resolution of images during printing would normally be improved. However, any significant reduction in paper brightness would mean that there would also be a poor contrast between the paper and image.

It would therefore be desirable to provide a paper sizing composition which imparts significantly improved hydrophobicity and printability characteristics and yet does not significantly reduce the brightness of the paper or board.

Thus a method of sizing paper or paper board is provided wherein a composition (A) is applied to at least one of,

- i) the surface of a formed paper or paper board sheet,
 - ii) a paper or paper board making cellulosic suspension prior to draining,
- wherein the composition (A) comprises an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix, comprising characterised in that an oligomer formed

from a monomer blend comprised of ethylenically unsaturated monomer or ethylenically unsaturated monomer blend,

(a) (meth)acrylamide and

(b) an organic mercaptan or organic sulphone,

is located at the surface of the polymer particles.

It has been found that the application of composition (A) to a paper making stock prior to draining on the machine wire produces effective internally sized paper. The composition (A) may be applied as the neat polymer dispersion as a single addition to the paper making stock or may be combined with for instance the retention, drainage aids or strength aids. Often it is preferred to apply the composition as a formulation in pre cooked starch. Typically the formulation would comprise 90-99.5 weight % starch and 0.5-10 weight % polymer particles, preferably 92.5-97.5 weight % starch and 2.5-7.5 weight % polymer particles, more preferably 95-97.5 weight % starch and 2.5-5 weight % polymer particles, based on total dry weight of starch and polymer particles. It has surprisingly been found that the composition can be used to form internally sized paper with superior properties.

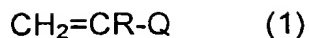
Composition (A) is particularly suited for surface sizing of paper and provides unique properties to the paper. Incorporated in the method of sizing paper or board composition (A) is applied to the surface of a formed sheet of paper or paper board. Often it is preferred to apply the composition as a formulation in pre cooked starch. Typically the formulation would comprise 90-99.5 weight % starch and 0.5-10 weight % polymer particles, preferably 92.5-97.5 weight % starch and 2.5-7.5 weight % polymer particles, more preferably 95-97.5 weight % starch and 2.5-5 weight % polymer particles, based on total dry weight of starch and polymer particles. Although the composition (A) would be desirably applied as a blend with starch it may also be applied as a neat aqueous dispersion of polymer particles. In addition to combining composition (A) with starch it may also be desirable to combine other ingredients normally applied during surface sizing, for instance Optical Brightening Agents (OBA). Normally the neat composition is applied at the size press in order to achieve maximum benefits of the sizing method disclosed herein.

Preferably in the method of sizing paper and paper board the composition comprises an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix and at the surface an oligomer formed from a monomer blend comprising,

- (a) (meth)acrylamide,
- (b) an organic mercaptan or organic sulphone,
- (c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group and
- (d) optionally other monomers.

The oligomer comprised in the composition used in the method of sizing paper may incorporate any organic mercaptan or organic sulphone but is preferably C₁₋₂₀ optionally substituted alkyl mercaptans, C₁₋₂₀ optionally substituted alkyl sulphones, optionally substituted C₅₋₇ cycloalkyl mercaptans, optionally substituted aromatic mercaptans, optionally substituted C₅₋₇ cycloalkyl sulphones or optionally substituted aromatic sulphones are preferred. More preferred are C₈₋₂₀ alkyl mercaptans, C₅₋₇ cycloalkyl mercaptans, aromatic mercaptans, C₈₋₂₀ alkyl sulphones, C₅₋₇ cycloalkyl sulphones or aromatic sulphones. Particularly preferred is either dodecyl mercaptan or dodecyl sulphone. Suitable substituted alkyl mercaptans include 3-mercaptopropanoic acid, 2-mercaptoethanol whilst 2-sulphonylethanol and 3-sulphonylpropanoic acid are suitable substituted alkylsulphones. The amount of organic mercaptan or organic sulphone used in the oligomer is normally up to 10 mole %. It may be possible to use more than one organic mercaptan and/or organic sulphone in the preparation of the oligomer, although the combined molar proportions of organic mercaptan(s) and/or organic sulphone(s) is generally up to 10 mole %. Preferably the level of organic mercaptan or organic sulphone compounds is in the range 2.5-5 mole %.

In the method of sizing paper or board the oligomer comprises any of ethylenically unsaturated tertiary amine or quaternary ammonium compounds into the oligomer, but preferred compounds are represented by compounds formula (1)



wherein

Q is $-\text{C}(\text{O})-\text{Z}-\text{A}$, $-\text{CH}_2-\text{N}^+\text{R}_1\text{R}_3\text{CH}_2\text{CR}=\text{CH}_2 \text{X}^-$ or $-\text{CH}_2 \text{NR}_1\text{CH}_2\text{CR}=\text{CH}_2$,

Z is $-\text{O}-$ or $-\text{NH}-$,

A is $-\text{C}_n\text{H}_{2n}-\text{B}$,

n is an integer from 1 to 4,

B is $-\text{NR}_1\text{R}_2$ or $-\text{N}^+\text{R}_1\text{R}_2\text{R}_3 \text{X}^-$,

R is $-\text{H}$ or $-\text{CH}_3$,

R_1 is C_{1-4} alkyl,

R_2 is C_{1-4} alkyl,

R_3 is $-\text{H}$ or C_{1-8} alkyl, C_{5-7} cycloalkyl or benzyl, and

X^- is anion, preferably halide, most preferably chloride.

Preferred ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds include for instance dimethylaminoethyl (meth)acrylate, acid addition salt or quaternary ammonium salt thereof, preferably dimethylaminoethyl (meth)acrylate, methyl chloride quaternary ammonium salt or dimethylaminoethyl (meth)acrylate, benzyl chloride quaternary ammonium salt.

Normally the level of ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds to be incorporated into the oligomer

is up to 10 mole %. Preferably these compounds are present in the oligomer in amounts in the range 2.5-5 mole %.

The oligomer compound normally contains higher levels of acrylamide or methacrylamide components. For instance the molar proportion of (meth)acrylamide is usually at least 85 mole % and is preferably at least 90 mole %. Typically the molar proportion of (meth)acrylamide is between 90 and 97.5 mole %, preferably 92.5-95 mole %.

It is also possible incorporate other ethylenically unsaturated monomers into the oligomer. In particular it is possible to incorporate up to 10 mole % ethylenically unsaturated carboxylic acid or ethylenically unsaturated carboxylic anhydride. This may be for instance acrylic acid or maleic anhydride preferably used in an amount between 2.5 and 5 mole %.

In the method of sizing paper the composition applied to the surface of the paper or board sheet further comprises polymeric particles are comprised of ethylenically unsaturated monomer or ethylenically unsaturated monomer blend, which monomer or monomer blend are substantially water insoluble at room temperature. The monomers polymerise to provide polymers that are substantially water insoluble at room temperature. Desirably the monomer or monomer blend has a solubility in water at 25°C of less than 5%. The monomers may be an ester of an ethylenically unsaturated carboxylic acid, styrene, alkyl styrene, (meth)acrylonitrile, vinyl carboxylate etc.. Typically the matrix of the polymeric particles are formed from a monomer or a monomer blend comprising monomers selected from the group consisting of styrene, C₁₋₁₂ alkyl (meth)acrylate, vinyl acetate, acrylonitrile. Preferably the matrix of the polymer particles is formed from 25-75 weight % monomer or monomer blend selected from any of styrene, acrylonitrile, vinyl acetate or C₁₋₂ alkyl (meth) acrylate, preferably styrene, acrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate, vinyl acetate and 25-75 weight % monomer or monomer blend selected from any C₃₋₁₂ alkyl (meth)acrylates, preferably butyl acrylate, n-hexyl acrylate, n-octyl acrylate and 2-ethylhexyl acrylate. More preferably the matrix of the

polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % styrene and 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % 2-ethylhexyl acrylate. In another preferred aspect the polymer particles have a minimum film forming temperature of between -5 and 55°C, preferably between 25 and 45°C, most preferably about 35°C. It may also be desirable to combine cross linking monomer into the monomer blend. The cross linking monomer can be any polyethylenically unsaturated monomer, for instance divinyl benzene, ethylene glycol dimethacrylate or triallyl amine. Typically the amount of cross linking monomer used would be below 1% by weight based on total weight of monomer, for instance in the range 0.25-0.50 weight %. Generally the composition used in the method of sizing paper or board comprises polymer particles which have a particle size in the range 80-200nm, preferably 100-120nm.

In the method of sizing paper the blend of starch and polymer particles would be applied to the surface of the formed sheet of paper at a dose of up to 20g/m², preferably up to 10g/m², typically around 3g/ m².

The method of sizing paper or paper board provides paper with good water resistance properties in combination with surprisingly high levels of paper brightness. Furthermore, the size can conveniently be applied in sizing formulations of pH from as low as 1 to as high as 12 and still provide acceptable results.

A further aspect of the invention includes a method of improving the printability of a sheet of paper by applying to the surface of the formed sheet of paper a composition comprising an oligomer formed from a monomer blend comprising,

- (a) (meth)acrylamide,
- (b) an organic mercaptan or organic sulphone,
- (c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, and
- (d) optionally other monomers.

In the method of improving printability of paper the oligomer would be applied directly to the formed sheet of paper at a dose of up to 20g/m^2 , preferably up to 10g/m^2 , typically around 3g/m^2 .

In the method of improving the printability of a sheet of paper, the oligomer, comprised in the composition may comprise any organic mercaptan or organic sulphone, generally C_{1-20} optionally substituted alkyl mercaptans, C_{1-20} optionally substituted alkyl sulphones, optionally substituted C_{5-7} cycloalkyl mercaptans, optionally substituted aromatic mercaptans, optionally substituted C_{5-7} cycloalkyl sulphones or optionally substituted aromatic sulphones are preferred. More preferred are C_{8-20} alkyl mercaptans, C_{5-7} cycloalkyl mercaptans, aromatic mercaptans, C_{8-20} alkyl sulphones, C_{5-7} cycloalkyl sulphones or aromatic sulphones. Particularly preferred is either dodecyl mercaptan or dodecyl sulphone.

In the method of improving printability the amount of organic mercaptan or organic sulphone used in the oligomer used in the composition is normally up to 10 mole %. It may be possible to use more than one organic mercaptan and/or organic sulphone in the preparation of the oligomer, although the combined molar proportions of organic mercaptan(s) and/or organic sulphone(s) is generally up to 10 mole %. Preferably the level of organic mercaptan or organic sulphone compounds is in the range 2.5-5 mole %. Preferably the oligomer used in the paper sizing composition comprises C_{8-20} alkyl mercaptans, C_{5-7} cycloalkyl mercaptans, aromatic mercaptans, C_{8-20} alkyl sulphones, C_{5-7} cycloalkyl sulphones or aromatic sulphones. Suitable substituted alkyl mercaptans include 3-mercaptopropanoic acid, 2-mercaptoethanol whilst 2-sulphonylethanol and 3-sulphonylpropanoic acid are suitable substituted alkylsulphones. Most preferably the paper sizing composition comprises an oligomer comprising either dodecyl mercaptan or dodecyl sulphone. The oligomer incorporated in paper sizing composition comprises the organic mercaptan or organic sulphone in an amount up to 10 mole %, preferably 2.5-5 mole %.

In the method of improving the printability of paper or board the oligomer comprises ethylenically unsaturated tertiary amine or quaternary ammonium compounds into the oligomer, but preferred compounds are represented by compounds formula (1) given before in the specification and wherein the same preferences apply.

Preferred ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds include for instance dimethylaminoethyl (meth)acrylate, acid addition salt or quaternary ammonium salt thereof, preferably dimethylaminoethyl (meth)acrylate, methyl chloride quaternary ammonium salt or dimethylaminoethyl (meth)acrylate, benzyl chloride quaternary ammonium salt.

In the method of improving the printability of paper the oligomer would preferably comprise ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds to be incorporated into the oligomer is up to 10 mole %. Preferably these compounds are present in the oligomer in amounts in the range 2.5-5 mole %. The oligomer compound normally contains higher levels of acrylamide or methacrylamide components. For instance the molar proportion of (meth)acrylamide is usually at least 85 mole % and is preferably at least 90 mole %. It is also possible to incorporate other ethylenically unsaturated monomers into the oligomer. In particular it is possible to incorporate up to 10 mole % other ethylenically unsaturated monomers into the oligomer. In particular it is possible to incorporate up to 10 mole % ethylenically unsaturated carboxylic acid or ethylenically unsaturated carboxylic anhydride. This may be for instance acrylic acid or maleic anhydride preferably used in an amount between 2.5 and 5 mole %.

In a particularly preferred method of improving printability of paper the oligomer is comprised in an aqueous dispersion of polymer particles. The oligomer would be present at the surface of the polymer particles wherein the matrix of the polymer particles are derived from ethylenically unsaturated monomer or ethylenically unsaturated monomer blend, which monomer or monomer blend are substantially water insoluble at room temperature. The monomers polymerise to provide polymers that are substantially water insoluble at room temperature. Typically the matrix of the

polymeric particles are formed from a monomer or a monomer blend comprising monomers selected from the group consisting of styrene, C₁₋₁₂ alkyl (meth)acrylate, vinyl acetate, acrylonitrile. Preferably the matrix of the polymer particles is formed from 25-75 weight % monomer or monomer blend selected from any of styrene, acrylonitrile, vinyl acetate or C₁₋₂ alkyl (meth)acrylates, preferably styrene, acrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate, vinyl acetate and 25-75 weight % monomer or monomer blend selected from any of C₃₋₁₂ alkyl (meth)acrylates, preferably n-butyl acrylate, n-hexyl acrylate, n-octyl acrylate and 2-ethylhexyl acrylate. More preferably the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % styrene and 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % 2-ethylhexyl acrylate. In another preferred aspect the polymer particles have a minimum film forming temperature of between -5 and 55°C, preferably between 25 and 45°C, most preferably about 35°C. Generally the composition used in the method of sizing paper or board comprises polymer particles which have a particle size in the range 80 to 200nm, preferably 100-120nm.

In a preferred method of improving the printability of paper a blend of starch and an aqueous dispersion of polymeric particles of particle size up to 1 micron, preferably 80-200nm, more preferably 100-120nm, wherein the polymeric particles comprise a water insoluble polymer matrix characterised in that an oligomer formed from a monomer blend comprising,

- (a) (meth)acrylamide,
- (b) an organic mercaptan or organic sulphone,
- (c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group and
- (d) optionally other monomers

and an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group comprises one or more compounds of formula (1) given before in the specification and wherein the same preferences apply.

Typically in the method of improving printability of paper the oligomer comprised in the composition applied to the surface of the formed sheet of paper comprises the compound of formula (1) in an amount up to 10 mole %, preferably 2.5-5 mole %. Ideally the oligomer is formed from a monomer blend comprising one or more compounds selected from the list comprising dimethylaminoethyl (meth)acrylate, acid addition salt or quaternary ammonium salt thereof, preferably dimethylaminoethyl (meth)acrylate, methyl chloride quaternary ammonium salt or dimethylaminoethyl (meth)acrylate, benzyl chloride quaternary ammonium salt. Preferably the oligomer formed from a monomer blend comprising acrylamide or methacrylamide in an amount of at least 85 mole %, preferably at least 90 mole %. The oligomer incorporated in the paper sizing composition may comprise as an additional ethylenically unsaturated monomer. In particular it is possible to incorporate up to 10 mole % ethylenically unsaturated carboxylic acid or ethylenically unsaturated carboxylic anhydride. This may be for instance acrylic acid or maleic anhydride preferably used in an amount between 2.5 and 5 mole %.

The invention relates to a method of improving printability of paper by applying to the surface of the paper a blend comprising starch, optionally optical brighteners and an aqueous dispersion of the polymeric particles which are formed from a monomer or a monomer blend comprising monomers selected from the group consisting of styrene, C₁₋₁₂ alkyl (meth)acrylate, vinyl acetate and acrylonitrile. Preferably the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight %, monomer or monomer blend selected from the group consisting of styrene, acrylonitrile, vinyl acetate and C₁₋₂ alkyl (meth)acrylates, preferably styrene, acrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate, vinyl acetate and 25-75 weight %, preferably 35-65 weight %, most preferably about 50 weight %, monomer or monomer blend selected from any of C₃₋₁₂ alkyl (meth)acrylates, preferably n-butyl acrylate, n-hexyl acrylate, n-octyl acrylate and 2-ethylhexyl acrylate. Most preferably the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % styrene and 25-75 weight %, preferably 35-65 weight %, most preferably about 50 weight % 2-ethylhexyl acrylate.

The method of improving printability of paper desirably involves applying to the surface of a formed sheet of paper a blend of starch and polymer particles that have a minimum film forming temperature of between -5 and 55°C , preferably between 25 and 45°C , most preferably about 35°C . The polymer particles comprised in the paper sizing composition desirably have a particle size below 1 micron, preferably in the range 80 to 200nm, more preferably 100-120nm. Ideally the blend of starch and polymer particles, comprise 0.5 to 10 wt % polymer particles and 90 to 99.5 wt.% starch, based on dry weight of the blend.

In the method of improving printability the blend of starch and polymer particles would be applied to the surface of the formed sheet of paper at a dose of up to $20\text{g}/\text{m}^2$, preferably up to $10\text{g}/\text{m}^2$, typically around $3\text{g}/\text{m}^2$.

In the method of improving printability of paper, it has surprisingly been found that the paper treated by this method has an acceptable level of water resistance in combination with a high degree of paper brightness and when used in for instance non-impact printing, provides superior printability properties. Furthermore, the size can conveniently be applied in sizing formulations of pH from as low as 1 to as high as 12 and still provide acceptable results.

One aspect the invention encompasses a novel composition comprising an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix and at the surface an oligomer formed from a monomer blend comprising,

- (a) (meth)acrylamide,
- (b) an organic mercaptan or organic sulphone,
- (c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group and
- (d) optionally other monomers.

Although any organic mercaptan or organic sulphone may be present in the oligomer, generally C₁₋₂₀ optionally substituted alkyl mercaptans, C₁₋₂₀ optionally substituted alkyl sulphones, optionally substituted C₅₋₇ cycloalkyl mercaptans, optionally substituted aromatic mercaptans, optionally substituted C₅₋₇ cycloalkyl sulphones or optionally substituted aromatic sulphones are preferred. Suitable substituted alkyl mercaptans include 3-mercaptopropanoic acid, 2-mercaptoethanol whilst 2-sulphonylethanol and 3sulphonylpropanoic acid are suitable substituted alkylsulphones. More preferred are C₈₋₂₀ alkyl mercaptans, C₅₋₇ cycloalkyl mercaptans, aromatic mercaptans, C₈₋₂₀ alkyl sulphones, C₅₋₇ cycloalkyl sulphones or aromatic sulphones. Particularly preferred is either dodecyl mercaptan or dodecyl sulphone.

The amount of organic mercaptan or organic sulphone used in the oligomer is normally up to 10 mole %. It may be possible to use more than one organic mercaptan and/or organic sulphone in the preparation of the oligomer, although the combined molar proportions of organic mercaptan(s) and/or organic sulphone(s) is generally up to 10 mole %. Preferably the level of organic mercaptan or organic sulphone compounds is in the range 2.5 to 5 mole %.

It would be possible to incorporate any number of ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds into the oligomer, but preferred compounds are represented by compounds of formula (1) given before in the specification and wherein the same preferences apply.

Preferred ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds include for instance dimethylaminoethyl (meth)acrylate, acid addition salt or quaternary ammonium salt thereof, preferably dimethylaminoethyl (meth)acrylate, methyl chloride quaternary ammonium salt or dimethylaminoethyl (meth)acrylate, benzyl chloride quaternary ammonium salt.

Normally the level of ethylenically unsaturated tertiary amine or ethylenically unsaturated quaternary ammonium compounds to be incorporated into the oligomer

is up to 10 mole %. Preferably these compounds are present in the oligomer in amounts in the range 2.5 to 5 mole %.

The oligomer compound normally contains higher levels of acrylamide or methacrylamide components. For instance the molar proportion of (meth)acrylamide is usually at least 85 mole % and is preferably between 90 mole % and 97.5 mole %, preferably 92.5 mole % to 95 mole %.

It is also possible to incorporate other ethylenically unsaturated monomers into the oligomer. In particular it is possible to incorporate up to 10 mole % ethylenically unsaturated carboxylic acid or ethylenically unsaturated carboxylic anhydride. This may be for instance acrylic acid or maleic anhydride preferably used in an amount between 2.5 and 5 mole %.

Generally speaking the matrix of the polymeric particles are comprised of ethylenically unsaturated monomer or ethylenically unsaturated monomer blend, which monomer or monomer blend is substantially water insoluble at room temperature. The monomers polymerise to provide polymers that are substantially water insoluble at room temperature. Typically the matrix of the polymeric particles are formed from a monomer or a monomer blend comprising monomers selected from the group consisting of styrene, C₁₋₁₂ alkyl (meth)acrylate, vinyl acetate, acrylonitrile. Preferably the matrix of the polymer particles is formed from 25-75 weight % monomer or monomer blend selected from any of styrene, acrylonitrile, vinyl acetate or C₁₋₂ alkyl (meth)acrylates, especially styrene, acrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate and vinyl acetate and 25-75 weight % monomer or monomer blend selected from any of C₃₋₁₂ alkyl (meth)acrylates, especially butyl acrylate, n-hexyl acrylate, n-octyl acrylate and 2-ethylhexyl acrylate. More preferably the matrix of the polymer particles is formed from 25-75 weight %, preferably 35 to 65 weight %, most preferably about 50 weight % styrene and 25-75 weight %, preferably 35 to 65 weight %, most preferably about 50 weight % 2-ethylhexyl acrylate. In another preferred aspect the polymer particles have a minimum film forming temperature of between -5 and 55°C, preferably between 25

and 45°C, most preferably about 35°C. Generally the composition comprises a dispersion of polymer particles which have a particle size in the range 80-200nm, preferably 100-120nm.

Thus the invention encompasses an aqueous dispersion of polymer particles, wherein the polymer particles have a particle size in the range 80-200nm, preferably 100-120nm and comprising a matrix of water insoluble polymer, preferably formed from ethylenically unsaturated water insoluble monomers, more preferably formed from 25-75 wt.%, usually around 50 wt.%, of one or more monomers selected from styrene, acrylonitrile, methyl methacrylate, vinyl acetate, especially styrene and 25-75 wt.%, usually around 50 wt.%, of one or more monomers selected from butyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate and n-octyl acrylate, especially 2-ethylhexyl acrylate, characterised in that the polymer particles also comprise at their surface an oligomer of acrylamide or methacrylamide which additionally comprises an organic mercaptan or organic sulphone, preferably a C₈₋₂₀ alkyl mercaptan or C₈₋₂₀ alkyl sulphone, more preferably dodecyl mercaptan or dodecyl sulphone. Preferably the oligomer also comprises components based on ethylenically unsaturated tertiary amines or ethylenically unsaturated quaternary ammonium compounds, for instance dimethylaminoethyl methacrylate methyl chloride quaternised or dimethylaminoethyl methacrylate benzyl chloride quaternised. It is also possible to incorporate other ethylenically unsaturated monomers into the oligomer. In particular it is possible to incorporate up to 10 mole % ethylenically unsaturated carboxylic acid or ethylenically unsaturated carboxylic anhydride. This may be for instance acrylic acid or maleic anhydride preferably used in an amount between 2.5 and 5 mole %.

The novel composition could be used in the coating of various substrates, but the compositions are desirably paper and paper board sizing agents or paper coating materials that can improve water resistance and/or printability of paper. Generally the novel compositions are blended with other materials such as solutions of natural or synthetic water soluble or water swellable polymers to form sizing or coating formulations.

The oligomer is made by mixing together the components with water and optionally other solvents, for instance alcohols such as ethanol or carboxylic acids such as acetic acid, wherein the components comprise at least

(a) (meth)acrylamide and

(b) an organic mercaptan or organic sulphone

and effecting oligomerisation in the usual manner.

A preferred form of the oligomer comprises the components

(a) (meth)acrylamide,

(b) an organic mercaptan or organic sulphone,

(c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group and

(d) optionally other monomers

are mixed with sufficient water and optionally an alcohol, for instance ethanol, and optionally a carboxylic acid, such as acetic acid, to provide an aqueous solution of the monomer blend. Oligomerisation is effected by the use of suitable initiators in the usual manner.

Oligomers formed from any of the organic mercaptans, may be treated with a suitable oxidising agent, for instance a peroxide, especially hydrogen peroxide, in order to convert some or all of the mercapto groups to sulphone groups.

Preparation of the aqueous dispersion of polymeric particles according to the invention may desirably be effected by suspension polymerisation or emulsion polymerisation. In a preferred process the water insoluble monomers, are emulsified into an aqueous medium comprising the oligomer in an amount up to 30 % by weight, preferably between 10 and 20% by weight. Polymerisation is effected in the usual way, but may for instance employ the use of redox initiators, thermal initiators, UV radiation or combinations of these. The composition formed will comprise an aqueous dispersion of polymeric particles of particle size up to 1 micron, preferably in the range 80-200 nm, more preferably in the range 100-120nm wherein the

polymeric particles comprise a water insoluble polymer matrix wherein the polymeric particles comprise a water insoluble polymer matrix and at the surface an oligomer formed from a monomer blend comprising,

- (a) (meth)acrylamide and
- (b) an organic mercaptan or organic sulphone

In a preferred form of the composition the oligomer is formed from a monomer blend comprising,

- (a) (meth)acrylamide,
- (b) an organic mercaptan or organic sulphone,
- (c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group and
- (d) optionally other monomers.

The following are examples of the invention.

Example 1

Preparation of Polymer A

45 parts by weight of styrene and 45 parts by weight of 2-ethylhexyl acrylate is emulsified in 125 parts by weight of water containing 10 parts by weight of an oligomer formed from 20 molar parts acrylamide and 1 molar part dodecyl mercaptan and oligomerised in a 50/50 wt/wt water/ethanol medium. Emulsion polymerisation is effected in the usual manner using redox initiators and a thermal initiator to form a stable dispersion of polymer particles.

Preparation of Polymer B

The process of preparing polymer A is repeated except the oligomer used comprises 19 parts by mole acrylamide, 1 part by mole dodecyl mercaptan and 1 part by mole part of the methyl chloride quaternary ammonium salt of dimethylaminoethyl methacrylate.

Preparation of Polymer C

The process for preparing polymer A is repeated except the oligomer used comprises 19 parts by mole acrylamide, 1 part by mole dodecyl mercaptan and 1 part by mole of methyl chloride quaternary ammonium salt of dimethylaminoethyl methacrylate.

Preparation of Polymer D

The process of preparing polymer A is repeated except the oligomer is prepared in a 50/50 wt/wt water acetic acid solvent.

Preparation of Polymer E

The process for preparing polymer D is repeated except the oligomer used comprises 90 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan and 5 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer F

The process for preparing polymer D is repeated except the oligomer used comprises 92.5 parts by mole acrylamide, 2.5 parts by mole dodecyl mercaptan and 5 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer G

The process for preparing polymer D is repeated except the oligomer used comprises 85 parts by mole acrylamide, 10 parts by mole dodecyl mercaptan and 5 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer H

The process for preparing polymer D is repeated except the oligomer used comprises 93.5 parts by mole acrylamide, 1.5 parts by mole dodecyl mercaptan and 5 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer I

The process for preparing polymer D is repeated except the oligomer used comprises 92.5 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan and 2.5 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer J

The process for preparing polymer D is repeated except the oligomer used comprises 95 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan.

Preparation of Polymer K

The process for preparing polymer D is repeated except the oligomer used comprises 80 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan and 15 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer L

The process for preparing polymer D is repeated except the oligomer used comprises 85 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan and 10 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer M

The process for preparing polymer D is repeated except the oligomer used comprises 90 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan and 5 parts by mole of dimethylaminoethyl methacrylate.

Preparation of Polymer N

The process for preparing polymer D is repeated except the oligomer used comprises 85 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan, 5 parts by mole of dimethylaminoethyl methacrylate and 5 parts by mole acrylic acid.

Preparation of Polymer O

The process for preparing polymer D is repeated except the oligomer used comprises 82.5 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan, 5 parts by mole of dimethylaminoethyl methacrylate and 7.5 parts by mole acrylic acid.

Preparation of Polymer P

The process for preparing polymer D is repeated except the oligomer used comprises 87.5 parts by mole acrylamide, 5 parts by mole dodecyl mercaptan, 5 parts by mole of dimethylaminoethyl methacrylate and 2.5 parts by mole acrylic acid.

Preparation of Polymer Q

The process for preparing polymer N is repeated except that a monomer blend comprising 63 parts by weight of styrene and 27 parts by weight of 2-ethylhexyl acrylate.

Preparation of Polymer R

The Process of preparing polymer Q is repeated except 20 weight % of the oligomer is used.

Preparation of Polymer S

The process of preparing polymer R is repeated except that 0.25 weight % ethyleneglycol dimethacrylate is combined with the styrene/2-ethylhexyl acrylate monomer blend.

Preparation of Polymer T

The process of preparing polymer R is repeated except that 0.50 weight % ethyleneglycol dimethacrylate is combined with the styrene/2-ethylhexyl acrylate monomer blend.

Preparation of Polymer U

The process of preparing polymer R is repeated except that 0.25 weight % divinyl benzene is combined with the styrene/2-ethylhexyl acrylate monomer blend.

Preparation of Polymer V

The process for preparing polymer Q is repeated except the oligomer used is prepared using 5 parts by mole maleic anhydride is used in place of acrylic acid.

Example 2

Polymers from example 1 are blended with a pre cooked aqueous 6% starch slurry at a ratio of 40:1 starch/polymer to provide a sizing formulation. The sizing formulations are applied to the surface of the paper standard unsized linerboard using a size press with a No. 7 K-bar to give a 5gm^{-2} coat and dried for 30 minutes at 110°C in an oven are made by blending each of the polymers of example 1 with a pre cooked starch solution to provide a blend comprising a ratio of 40:1 starch:polymer. The sheets are assessed for a 60 second Cobb test and the results are shown in Table 1.

Table 1

Polymer	Average Cobb Test gm ⁻²
A	22.1
D	17.2
E	22.6
F	22.0
G	25.9
H	24.1
I	21.5
J	21.3
K	23.8
L	22.5
M	21.8
N	25.6
O	25.1
Q	21.6
R	20.2
S	19.6
T	20.1
U	19.1
V	20.9

As can be seen from the results all of the products give acceptable water resistance to the sheet. Particularly good results are obtained from formulations comprising polymers B, I, J, M, Q, R, S, T, U and V

Example 3

Polymers from example 1 are blended with an aqueous 6% starch slurry at a ratio of 20:1 starch/polymer. The blends are coated onto UMIST paper sheets at a dose of 5gm⁻². Printability tests are obtained using a Hewlett Packard Deskjet 560C printer.

The Black Optical Density and Colour Density were measured on paper coated using the respective products. The results are presented in Table 2

OD - Optical Density

CD - Colour Density

Deskjet is a trade mark of Hewlett Packard.

Table 2

POLYMER	CD Cyan	CD Green	CD Yellow	CD Blue	CD Magenta	CD Red	Pass/ Fail	Com Black OD min
A	2	2	1	4	1	1	Pass	1.386
B	2	2	0	4	1	1	Pass	1.332
C	2	2	0	3	1	1	Pass	1.356
D	2	3	0	3	1	1	Pass	1.39
N	2	2	1	4	1	2	Pass	1.412
O	2	2	1	4	1	2	Pass	1.420
P	2	2	1	4	1	2	Pass	1.430
Q	2	1	2	-1	1	2	Pass	1.353

As can be seen all of the polymers gave acceptable results.

Example 4

The 20:1 starch/polymer formulations of example 3 are coated onto UMIST standard paper sheets and standard brightness tests are carried out. The results of the tests are shown in Table 3.

Table 3

Surface Size	Brightness
Starch only	75.75
Starch + OBA + Polymer A	82.58
Starch + OBA + Polymer B	82.06
Starch + OBA + Polymer C	82.62
Starch + OBA + Polymer D	82.63
Starch + OBA + Polymer I	81.0
Starch + OBA + Polymer J	80.6
Starch + OBA + Polymer K	81.1
Starch + OBA + Polymer L	81.3
Starch + OBA + Polymer M	81.5
Starch + OBA + Polymer N	83.39

The polymers of the current invention gave a high degree of brightness. Best results were obtained using polymers A,B,C,D and N.

Example 5

Polymers D and Q from example 1 are blended with a pre cooked aqueous 6% starch slurry at a ratio of 40:1 starch/polymer to provide various sizing formulation of different pHs. The sizing formulations are applied to the surface of the standard linerboard as in example 2. Water resistance of the sized paper is measured using 60 second Cobb test. The results are shown in Tables 4 and 5

Table 4

Formulation	Cobb Value (gm ⁻²)								
	pH 1.7	pH 2.9	pH 4.1	pH 5.8	pH 6.7	pH 7.6	pH 9.2	pH 10.2	pH 11.5
Polymer D	21.2	21.0	20.6	21.3	21.1	22.0	20.6	20.7	21.9

Table 5

	Cobb Value (gm ⁻²)					
Formulation	pH	pH	pH	pH	pH	pH
	1.5	3.6	7.1	9.2	10.3	11.7
Polymer Q	19	18.1	19.3	18.8	18.3	18.8

The results of this test demonstrate that the polymers provide the paper with good water resistance at acid, neutral or alkaline pHs.

Example 6

Polymer Q was added as the aqueous emulsion directly to two types of papermaking stock and the formed paper sheets were tested for water resistance.

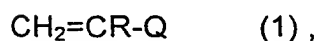
	Cobb Value (gm ⁻²)			
dose (Kg/T)	2	4	8	12
Waste Furnish	185	74	34	25
Fine Furnish	188	44	24	26

As can be seen the use of the polymers of the invention as internal sizing agents shows good water resistance properties on two different types of stock.

The results of all of these examples clearly demonstrate that the products of the invention provide paper with good water resistance, printability and brightness.

Claims

1. A method of sizing paper or paper board by applying a composition (A) to at least one of,
 - i) the surface of a formed paper or paper board sheet,
 - ii) a paper or paper board making cellulosic suspension prior to draining,
 wherein the composition (A) comprises an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix, comprised of ethylenically unsaturated monomer or ethylenically unsaturated monomer blend, characterised in that an oligomer formed from a monomer blend comprising,
 - (a) (meth)acrylamide and
 - (b) an organic mercaptan or organic sulphone,
 is located at the surface of the polymer particles.
2. A method according to claim 1 wherein component (b) is selected from the group consisting of C₈₋₂₀ alkyl mercaptans, C₅₋₇ cycloalkyl mercaptans, aromatic mercaptans, C₈₋₂₀ alkyl sulphones, C₅₋₇ cycloalkyl mercaptans and aromatic sulphones, preferably either dodecyl mercaptan or dodecyl sulphone.
3. A method according to claim 1 or claim 2 wherein the oligomer further comprises component (c) which is a compound of formula (1)



wherein

Q is $-\text{C}(\text{O})-\text{Z}-\text{A}-$, $-\text{CH}_2-\text{N}^+\text{R}_1\text{R}_3\text{CH}_2\text{CR}=\text{CH}_2 \text{ X}^-$ or $-\text{CH}_2 \text{ NR}_1\text{CH}_2\text{CR}=\text{CH}_2$,

Z is $-\text{O}-$ or $-\text{NH}-$,

A is $-\text{C}_n\text{H}_{2n}-\text{B}-$,

n is an integer from 1 to 4,

B is $\text{-NR}_1\text{R}_2$ or $\text{-N}^+\text{R}_1\text{R}_2\text{R}_3 \text{ X}^-$,

R is -H or -CH_3 ,

R_1 is C_{1-4} alkyl,

R_2 is C_{1-4} alkyl,

R_3 is -H or C_{1-8} alkyl, C_{5-7} cycloalkyl or benzyl, and

X^- is an anion, preferably halide, most preferably chloride.

4. A method according to any of claims 1 to 3 wherein component (c) is dimethylaminoethyl (meth)acrylate, acid addition salt or quaternary ammonium salt thereof, preferably dimethylaminoethyl (meth)acrylate, methyl chloride quaternary ammonium salt or dimethylaminoethyl (meth)acrylate or benzyl chloride quaternary ammonium salt.
5. A method according to any of claims 1 to 4 wherein the oligomer comprises at least 85 mole % of component (a), preferably at least 90 mole %.
6. A method according to any of claims 1 to 5 wherein the oligomer comprises component (b) in an amount up to 10 mole %, preferably 2.5 - 5 mole %.
7. A method according to any of claims 1 to 6 wherein the oligomer comprises component (c) in an amount up to 10 mole %, preferably 2.5 - 5 mole %.
8. A method according to any of claims 1 to 7 wherein the oligomer further comprises component (d) which is an ethylenically unsaturated carboxylic acid or an ethylenically unsaturated carboxylic anhydride in an amount up to 10 mole %.
9. A method according to claim 8 wherein component (d) is acrylic acid or maleic anhydride and is present in an amount between 2.5 and 5 mole %.
10. A method according to any of claims 1 to 9 wherein the matrix of the polymeric particles are formed from a monomer or a monomer blend comprising monomers

selected from the group consisting of styrene, C₁₋₁₂ alkyl (meth)acrylate, vinyl acetate and acrylonitrile.

11. A method according to any of claims 1 to 10 wherein the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight %, monomer or monomer blend selected from any of styrene, acrylonitrile, vinyl acetate and

C₁₋₂ alkyl (meth)acrylate, preferably styrene, acrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate, vinyl acetate and 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight %, monomer or monomer blend selected from any of C₃₋₈ alkyl (meth)acrylate, preferably butyl acrylate, n-hexyl acrylate, n-octyl acrylate and 2-ethylhexyl acrylate.

12. A method according to any of claims 1 to 11 wherein the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % styrene and 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % 2-ethylhexyl acrylate.

13. A method according to any of claims 1 to 12 wherein the polymer particles are formed from a monomer blend comprising cross linking monomer.

14. A method according to any of claims 1 to 13 wherein the polymer particles have a minimum film forming temperature of between -5 and 55°C, preferably between 25 and 45°C, most preferably about 35°C.

15. A method according to any of claims 1 to 14 wherein the polymer particles have a particle size in the range 80-200nm, preferably 100-120nm.

16. A method according to any of claims 1 to 15 wherein the composition (A) comprises 0.5 to 10 weight %, preferably 2.5 to 5 weight %, polymer particles and 90 to 99.5 weight %, preferably 95 to 97.5 weight %, starch based on total dry weight of polymer particles and starch.

17. A method of improving printability of a sheet of paper by applying to the surface of the formed paper sheet a composition comprising an oligomer formed from a monomer blend comprising,

(a) (meth)acrylamide,

(b) an organic mercaptan or organic sulphone,

- (c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, and
- (d) optionally other monomers.

18. A method according to claim 17 wherein the composition comprises an aqueous dispersion of polymeric particles of particle size up to 1 micron, preferably 80-200nm, wherein the polymeric particles comprise a water insoluble polymer matrix, preferably formed from styrene and 2-ethylhexyl acrylate, and the oligomer is located at the surface of the polymer particles.

19. A method according to claim 17 or claim 18 wherein the oligomer is formed from a monomer blend comprising,

- (a) 85-95 mole % (meth)acrylamide,
- (b) 2.5-10 mole % of an organic mercaptan or an organic sulphone, preferably dodecyl mercaptan or dodecyl sulphone,
- (c) 2.5-10 mole % of an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, preferably dimethylaminoethylmethacrylate, and
- (d) 0-10 mole% other ethylenically unsaturated monomers, preferably acrylic acid or maleic anhydride.

20. A method according to any of claims 17 to 19 wherein the composition comprises 0.5 to 10 weight %, preferably 2.5 to 5 weight %, polymer particles and 90 to 99.5 weight %, preferably 95 to 97.5 weight %, starch based on total dry weight of polymer particles and starch.

21. A method according to any of claims 17 to 20 wherein the composition comprises optical brightening aids.

22. A composition comprising an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix, preferably formed from styrene and 2-ethylhexyl acrylate, characterised in that an oligomer formed from a monomer blend comprising,

- (a) 85-95 mole % (meth)acrylamide and
- (b) 2.5-10 mole % of an organic mercaptan or an organic sulphone, and

- (c) 2.5-10 mole % of an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, and
- (d) 0-10 mole% other ethylenically unsaturated monomers, preferably acrylic acid or maleic anhydride,

is located at the surface of the polymer particles.

23. A composition according to claim 22, wherein the polymeric particles have a particle size of 80-200 nm.

24. A composition according to claim 22 or claim 23, wherein component (b) is dodecyl mercaptan or dodecyl sulphone, present in an amount of 2.5-5 mole % based on total oligomer.

25. A composition according to any of claims 22 to 24, wherein component (c) is dimethylaminoethyl methacrylate, present in an amount of 2.5-5 mole % based on total oligomer.

26. A composition according to any of claims 22 to 25, wherein component (d) is acrylic acid or maleic anhydride, present in an amount of 2.5-5 mole % based on total oligomer.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 00/00160

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21H23/02 D21H17/37 D21H17/41 C08F2/24 //D21H21/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	—	1, 17, 22
Y	DE 30 47 688 A (BASF AG) 22 July 1982 (1982-07-22) the whole document	1, 17, 22
A	—	3, 4, 7-12, 16, 18-20, 25, 26
	—	—

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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